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On Titanium, Thermite, the Bronze Age and... Drywall!

The process for extracting metals from their ores dates back to the Bronze Age. Despite many modifications, the Bronze Age method to extract copper and tin from their oxides, is basically still in use today for the mass-production of a wide variety of metals and alloys. In the step-by-step guide below I describe a method that allows to extract metallic titanium from white pigment, in your own backyard *and* using over-the-counter materials!*Where does the drywall come into it? Read on! And it works too, I've made nuggets of titanium in this way many times before.*

Homemade Titanium Metal from OTC materials in a Thermite Reaction:

One of the most used methods of extracting metals from their ores (usually oxides) is the chemical reduction of these oxides by means of a reducing agent, often carbon or another metal. This principle has been put to industrial use basically since the Bronze Age. Among these pyrometallurgical reductions, as they are known in chemical metallurgy, reductions with aluminium, referred to as aluminothermy, occupy a prominent class. Best known among these is what is colloquially referred to as Thermite reactions. The term*Thermite* (etymologically probably a contraction between *thermal* and*dynamite*, on account of the almost violent generation of lots and lots of heat during the process) actually originally specifically refers to the reaction of iron oxide with aluminium powder during which liquid iron and liquid alumina (aluminium oxide) are formed in a most spectacular fashion (see the many interesting YouTube videos). The worded reaction taking place is simply (right hand photo: a 400 g titanium thermite shortly after ignition):
Iron oxide + Aluminium ---> liquid Iron + liquid Aluminium Oxide (Alumina)
The convenient fact that both reaction products are generated in the molten state (thus allowing to obtain lump metal or even castings) is due to the fact that the reaction is accompanied by massive heat generation, sufficient to heat the reaction products to well above their respective melting points (3,730 F for alumina and 2,800 F for iron).
Today, iron is industrially hardly ever produced by aluminothermy but a whole array of more exotic metals and alloys is. And due to linguistic erosion, all aluminothermic processes (even those where iron plays no part) are now commonly referred to as *thermite reactions* or *thermite reductions*.

Metals (understood here as *chemical elements*) as diverse as vanadium, niobium, manganese, cobalt and chromium are industrially produced using aluminothermy. Alloys (binary or complex) of these but involving also iron, molybdenum, tungsten, tantalum, osmium and others can be produced similarly. Many other elements, including copper, silicon, boron, lead, tin, scandium, nickel, zinc and a whole raft of others are not usually prepared industrially in this way but can be (and have successfully been) produced by backyard scientists (like me).
Where does that leave the so far auspiciously absent titanium? Well, aluminothermic production of titanium metal is a slightly harder nut to crack (industrially the metal is prepared not from its oxide but from the tetrachloride, by means of reduction with magnesium - and not aluminium, in a process known as the Kroll process) because the reaction:
Titanium dioxide + Aluminium ---> Titanium + Alumina
does not generate enough heat for the reaction products to heat to above their respective melting points (the MP of titanium is 3,034 F), leaving the experimenter with a sintered mass of solid alumina, with solid, powdered titanium metal locked into the alumina matrix. Only melting the whole thing to well above 3,730 F, the MP of alumina, would make the recovery of lump titanium metal possible.

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There is of course a remedy to this problem and it's known in pyrometallurgical circles as *heat boosting*. Heat boosting is the technique whereby extra reaction heat is pumped into the reacting mix by running a second much hotter reaction simultaneously with the main reduction reaction, in the same reactor. In the case of aluminothermy, most usually a heat booster reaction is chosen that involves the oxidation of extra amounts of added aluminium powder with a powerful oxidiser. The worded reaction of the heat booster reaction is simply:
Oxidiser + Aluminium ---> Alumina + by-product
Oxidisers capable of oxidising aluminium with great generation of heat are a plenty (in fact, all the metal oxides suitable for thermite reductions are great oxidisers, it just so happens that titanium dioxide isn't very good on its own).
Commercially used heat booster oxidisers include chlorates, perchlorates, nitrates and sulphates (there are others, less frequently used).

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The oxidiser chosen for this particular method of backyard metal production is calcium sulphate, more commonly known as plaster of Paris, gypsum or... drywall or wall filler! The worded booster reaction is:
Calcium Sulphate + Aluminium ---> Calcium Sulphide + Alumina + much, much heat!
The mixture of calcium sulphide and alumina is usually referred to as the *slag*.
By combining the main reduction reaction (titanium dioxide + aluminium) with the booster reaction in the correct ratios, the required reaction temperature can be increased to almost any level, including that where all three reaction products (titanium metal, calcium sulphide and alumina) are produced above their melting points. From the post-reaction, hot, molten metal/slag mixture, the metal then coalesces out; much like oil separates out from an oil/vinegar salad dressing. After cooling, the metal (the most dense component of the mix) is then found at the bottom of the crucible, nicely protected by the slag from oxidation by air during the cooling step.
How to calculate these ratios is outside the scope of this guide but is usually referred to as a *thermochemical calculation*, which takes into account all the reaction enthalpies and the heat capacities of the reaction products and their abundance in the slag/metal mix and allows a precise calculation of the end-temperature of the post-reaction mixture.
So, in a nutshell, by combining the right amounts of titanium dioxide, calcium sulphate and aluminium and by igniting this mixture in a fire proof crucible solid titanium can be obtained (after cooling of the assembly, of course). So far, so good...

Formulation:

The precise composition of the mixture, here presented for a 100 g reaction batch, is (quantities in gram):
Titanium dioxide 30.0
Drywall 25.5
Aluminium powder 27.0
Ground fluorite 17.5
For different batch sizes, first calculate the batch factor (BF). For a batch of, say, 300 g, BF = 300 / 100 = 3. Now multiply the individual weights with the BF: 30.0 x 3 = 90.0 g, 25.5 x 3 = 76.5 g and so on. Finally check the result by adding the weights up: 90.0 + 76.5 + 81.0 + 52.5 = 300 g.
Fluorite here is the ingredient so far not discussed. Its role is that of a *slag fluidiser*. Where above I made the analogy of the metal coalescence from the molten slag/metal mix and the separation of oil and vinegar in a salad dressing, please note that this analogy is in fact very fair and quite accurate. To promote the separating of the metal from the molten sulphide/alumina mixture, it's beneficial to greatly improve its fluidity (reduce its viscosity in other words), as the coalescing metal droplets will find it much easier to sink through the molten cauldron and meet up.
Fluorite (chemically *calcium fluoride*) has a much lower melting point (2,555 F) than both alumina and calcium sulphide and is at those temperatures highly mobile, thereby lowering the viscosity of the melt considerably and keeping it fluid also somewhat longer. It's also completely chemically inert in these conditions, as aluminium is incapable of reducing this particular fluoride.

Weighing and dry-mixing of the formulation

Weigh the ingredients to at least three significant digits: for example 2.56 g, 10.3 g or 315 g.
Dry-mix the powders in a roomy container, typically a hermetically closed food container or similar, by shaking it. I like to include a couple of marbles in the container during mixing, as their sloshing about greatly improves mixing efficiency. Mix until a thoroughly homogeneous dry-mix is obtained, a few minutes should do the job, depending on batch size.
Wearing a dust protection mask during weighing and dry-mixing is probably advisable (although truth be told I never do).

Fit-for-purpose ingredients

Titanium dioxide:
A *good quality* grade of titanium dioxide, in the form of fine flour, of good, clean white colour is advisable. Exact granulometry isn't critical. If lumpy, sieve it with a tea strainer or such like. The lumps can later be recovered by gently grinding in a mortar and pestle.
Calcium sulphate:
Use a no-frills wall filler, the cheaper the better. High-end of the market products may contain additives to regulate setting speed or wetting behaviour that may (or may not) be somewhat

detrimental to the thermite process.
The wall filler needs to be thoroughly dried to drive off inevitable crystal water (this would otherwise be driven off during the reaction and that could lead to spattering or a porous slag metal mix) and to ensure it's made up mostly of *anhydrous calcium sulphate*. Dry at high heat for about two hours by spreading the product in an oven proof dish or stainless steel pan. Drying can be carried out (completely safely, wall filler isn't toxic) either in a kitchen oven (use max setting) or on the hob in a steel or copper pan on medium-high heat. The wall filler will probably darken slightly in colour: this is normal. After drying and cooling, store it in a dry, hermetically closed container (e.g. a rubber sealed pickling jar), where it will keep dry indefinitely. It is not particularly hygroscopic but will, if exposed, slowly pick up moisture from the air.
Aluminium powder:
The grade isn't critical. I would advise against too finely ground grades, about 200 - 400 mesh is what I use. Higher mesh (finer powder) may lead to too fast reactions and too high temperatures and hence a formulation adjustment may be required (see trouble shooting). And really coarse aluminium (shavings or turnings) would probably still work fine, provided really large (1 kg or more of mix) batches are used and you can get the bugger to ignite.

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Some pyrotechnical grades of aluminium powder, like German Black, contain significant amounts of carbon and may be less suitable.
Ground Fluorite:
Fineness isn't critical either. Something of the consistency of fine sand is great. There is no such thing as "too fine" Fluorite, as this species doesn't actually take part in the reactions but merely melts and increases the slag fluidity.
Reaction assembly
While the entire procedure has been designed with the safety of the experimenter in mind, it has to be noted that during reaction temperatures well in excess of 3,800 F are being generated, so keeping one's distance and some rudimentary insulation against these excessive heats are advisable (right hand photo: a 400 g titanium thermite assembly - magnesium ribbon not installed yet).
For this an embedded design is used, which consists of an of-the-shelf terracotta plant pot (of suitable size) filled with the thermite mixture, embedded in a larger container (another plant pot for instance) filled with (this is important) dry sand. Prior to filling the crucible plant pot with thermite mixture, close over the hole in the bottom with duct tape or similar. Pictures speak louder than words and here's such an assembly at work for a silicon thermite (a cache-pot and small steel bucket are used here).
The dry sand insulates the crucible (the sand will get pretty hot, depending on batch size) and holds it together during the reaction: the intense heat inevitably causes the plant pot to crack (but not melt) due to the extreme thermal shock the material is subjected to.
For smaller reactions, porcelain drinking cups or even egg cups as smaller crucibles are equally suitable.

Ignition method

Several ignition methods are available, from very safe to slightly riskier, but all involve locally heating the thermite

mixture to very high heat to ensure the mixture ignites and the reactions start (if you've ever heard the term*activation energy*, this is it).
My preferred one I've dubbed *ignition mix + magnesium ribbon*. It consists of separately preparing a small amount of a mixture of dried wall filler and aluminium powder (here the grade of aluminium needs to be sufficiently fine - 200 mesh or finer) in a weight ratio of wall filler/aluminium of 136 / 72. Prepare about 20 g or so and keep it in a safe place, hermetically sealed. This ignition mixture when ignited burns with sufficient heat to set alight even the most stubborn of thermite mixtures (some can be hard to light but the titanium/sulphate boosted thermite has never caused me such problems).
The ignition mix itself requires quite a bit of heat input to get going (which is why it's safe to store indefinitely) and the best way of doing this in my opinion is by means of magnesium ribbon. The ignition procedure thus becomes: after filling the pant pot with thermite mixture, make a small dent in it at the top and centre and fill this cavity with about 1 small teaspoon of ignition mix (adjust the amount for much smaller batches). Stick a 1" long piece of magnesium ribbon in the ignition mix. The magnesium ribbon can be lit with a small propane blow torch (like a pen blow torch - the ribbon will also light more easily if you cut a couple of small 1 mm cuts parallel to the length of the ribbon at the end to be lit). *Caution*, once the ribbon is lit, there is no going back: stand well back as the magnesium fuse will burn down and ignite the ignition mix and the burning ignition mix will ignite the thermite mixture...
Other experimenters use the potassium permanganate / glycerin ignition method, others simply take a blow torch straight to the thermite mix *or stick a fireworks sparkler in it*. Personally I prefer my own method, because it allows the experimenter to retreat to a safe distance without a great hurry and is relatively idiot-proof.

Energy produced

It's intuitive that something that delivers high melting products like titanium metal and alumina in the molten state must generate lots of heat. Well, a 500 g reaction mix delivers about 1,500 kJ (kilojoules), enough to heat about 9 liters of water from room temperature to boiling point. A domestic 600 W microwave oven would take nearly 45 minutes of operation on full power to achieve that. Industrial scale thermite reactions probably generate enough energy to keep a small town supplied with energy for a few minutes...

Recovery of the metal

Leave the assembly to cool down sufficiently for safe post-reaction handling. Lift the plant pot out of the sand insulator: the pot is usually seriously cracked but still held together by a layer of slag sticking to the inner wall.
Now break open the slag with a hammer: an annealed mixture of alumina, fluorite and calcium sulphide is pretty hard stuff, so considerable force may be needed depending on the size of the block of slag.
Inside you should find nuggets of titanium metal. With my sulphate-boosted reactions, the nuggets (or *reguli*, if you want to be posh) resemble small new potatoes because of their golden hue (the colour is due to a very thin layer of surface oxide) with some minor surface irregularities. A 20 g test batch will usually deliver a few nuggets a couple of mm across; a 100 g reaction already yields blobs the size of smallish marbles. Much larger reactions are likely to produce roundish slabs of metal.
Feel like a real metallurgist and calculate the obtained yield as follows. A 100 g of the mix contains 18.0 g of the metal (but as oxide, of course). Recover as much of the produced metal as possible, including smaller reguli and weigh it. The yield is calculated by dividing the weight of the recovered metal by the weight of the total metal contained in the batch and multiplying the result by 100 %.

Most of the 'missing' metal (100 % minus the yield) is in fact present in the slag as fine, even invisibly small droplets, stuck in some of the early formed slag that froze when it hit the cold crucible walls, this metal had no opportunity to settle out from the slag. (Photo left: a fresh 20 g thermite titanium button, after light buffing with sand paper.)

Yield usually improves greatly with the size of the reaction: for reactions of, say about 1 kg, I'd expect the yield to be well over 90 %.

Positive identification of the metal as actual titanium

1. Buff it up with sanding paper: removing the surface coating of oxide reveals the highly shiny, metallic nature of the material. Left alone the shiny surface will slowly tarnish again, forming a new layer of oxide. This process is known as *passivation* and protects the metal against further attack from air oxygen. It shares that property with aluminium (and other metals/elements).

2. Check electrical conductivity (press the electrodes against freshly sanded surface): the material conducts electricity, confirming its metallic nature.

3. Flame test: press a piece of the metal against a fast spinning sanding wheel or similar. Small fragments of the metal will be torn off and burn up spontaneously in the air. Nice to watch and fairly unique to titanium. Watch a video by my friend Jeffrey on the page below, using metal from a chlorate boosted reaction (my formulation). Scroll down to almost the bottom of the page.

4. Chemical identification: for this you'll need strong hydrochloric acid (HCl 20 w% or more - 30 w% is better) and some pharmacy or hair dye grade hydrogen peroxide (H_2O_2, a few w%). Crush up some of the metal with a hammer (due to contamination with oxygen and nitrogen it's rather brittle) and put it in a test tube or otherwise suitable glass container and immerse it in the acid for 24 h or so. As small amounts of hydrogen sulphide (rotten eggs gas - see below) will be formed, store the assembly in a well ventilated place, away from your living quarters.
Although titanium is well known and desired for its excellent corrosion resistance, strong hydrochloric acid does attack it noticeably but slowly even at ambient temperatures, with the ubiquitous evolution of hydrogen gas. Titanium (III) chloride ($TiCl_3$) is formed, which, depending on concentration has a beautiful, amethyst-like purple hue. After the overnight soak in HCl, carefully add a few drops of the hydrogen peroxide to the solution: a beautiful deep red, caused by a very characteristic red colour from a titanium (IV) peroxo complex being formed. A more detailed explanation can be found here.

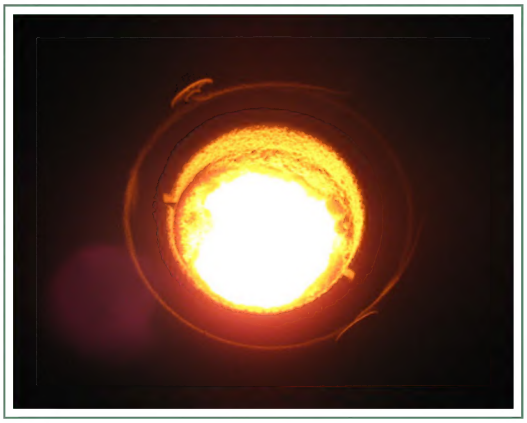
Below, from left to right three test tubes: titanium starting to react with strong HCl with bubbles of hydrogen starting to form (left), after some time of reaction the typical Amethyst purple of $TiCl_3$ appears (middle), after adding H_2O_2 to some liquid from the middle tube the deep red colour of the titanium (IV) peroxo complex confirms the presence of titanium (right).

Why does it smell slightly of rotten eggs?
The explanation is simple: the slag contains calcium sulphide and inevitably the metal (which in industrial circumstances would be de-slagged by re-melting under argon or in vacuum) contains small amounts of slag inclusions. Calcium sulphide, like most other sulphides, is prone to hydrolysis (it's attacked by water or moisture from the air) and this causes hydrogen sulphide (H_2S) to be formed according to:
Calcium Sulphide + Water (or acid) ---> Calcium Hydroxide (or Calcium salt) + Hydrogen Sulphide
To keep specimens of the metal without resorting to de-slagging, storage in hermetically sealed glass containers or ampoules is recommended, to allow admiring the metal without experiencing the faint but unmistakable smell of rotten eggs.
It's also advisable to dispose of the slag and broken crucible by either putting it in some disposable sealed container or

wrapping it amply in bin bags, before disposing of it in a domestic bin, to avoid the lingering smell of rotten eggs around the house.

Trouble shooting

I'll assume that in the case of problems, weighing, mixing and ignition were all carried out correctly, the correct ingredients were used and the thermite burned right through but that no metal or very poor quality metal was formed(right hand photo: the post-reaction melt of a 400 g titanium thermite reaction).



The most likely cause of poor metal production is not that the metal didn't form but that it didn't coalesce out of the slag/metal mix. The most likely reasons are either: reaction ran too cold or reaction ran too hot. The main cause of aberrant temperature behaviour is fineness of ingredients but this should be rectifiable by adjusting the overall formulation slightly.

Too cold: symptoms include:

- slag didn't collect well at bottom of crucible, contains considerable voids
- no metal can be found or metal is too intertwined with solid slag mass and cannot be broken away from slag. Excessive sticking of the metal to the solidified slag (good metal breaks away clean and easily).

This is indicative of too low reaction temperature, leading to too high slag viscosity. This problem should be remediable by increasing the amount of booster reaction. For the 100 g batch described above, increase the amount of dried wall filler to 30.6 g and the aluminium powder to 29.6 g (the total batch weight then becoming 107.7 g) and try again.

Too hot: symptoms include:

- highly porous slag, numerous bubble-like voids, an indication that something had started to volatilise
- no metal can be found or metal is too intertwined with solid slag mass and cannot be broken away from slag

The main reason of too high reaction temperatures can occur is the use of very fine ingredients: ingredient fineness in heterogeneous reactions to some extent regulates reaction speed and very fast reactions tend to lose, proportionately speaking, less heat to the environment and this can lead to overheating. At very high temperatures, even the most high boiling substances gain some degree of volatility. This evaporation can interfere with the metal coalescence, a bit like it would be hard for the oil in an oil/vinegar salad dressing to separate out, if the dressing was actually boiling.

Try and remedy this by reducing the amount of booster reaction. For the 100 g batch, use 20.4 g of dried wall filler (instead of 25.5 g) and 24.4 g of aluminium powder (instead of 27.0 g), making the total batch weight 92.3 g and try again.

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